



Biohybrids of twinning $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanoparticles and *Sporomusa ovata* for efficient solar-driven reduction of CO_2 to acetate

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ABSTRACT

Integration of microorganisms with semiconductors is an effective approach to sustainable solar-driven production of chemicals from CO_2 , which lies in the development of efficient, highly biocompatible, and low-cost photocatalysts. Herein, twinning $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanoparticles with long-range ordered homojunctions were synthesized and used for the first time in the construction of a biohybrid system ($\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$) with a non-photosynthetic acetogenic bacterium of *Sporomusa ovata*. The $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system yielded 49.33 ± 3.54 mM of acetate at a production rate of 8.22 ± 0.59 mM d^{-1} with a quantum efficiency of $16.82 \pm 1.21\%$ under illumination, which exceeded those of other reported biotic-abiotic hybrid systems. Further investigations revealed that the twin-induced homojunctions with staggered phase alignment contributed to enhance the separation efficiency of photogenerated electron-hole pairs and avoid photocorrosion of the photocatalyst. Due to the dual advantages of light absorption and biocompatibility of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$, the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system could efficiently harvest light energy and transfer photogenerated electrons to cellular metabolism, driving the Wood-Ljungdahl pathway to efficiently synthesize acetate from CO_2 under illumination.

1. Introduction

The consequence of excessive anthropogenic carbon emissions urgently requires the design of innovative strategies to develop carbon reduction and renewable energy technologies [1,2]. Photosynthesis is considered as one of the most desirable and sustainable strategies for CO_2 utilization. However, the naturally occurring transduction of solar energy into chemical bonds is too sluggish to keep pace with the needs of the modern society [3,4]. With advances in materials science, the quantum efficiency of the synthetic semiconductor photocatalysts often exceeds that of natural photosynthesis, but the artificial catalysts still struggle to replicate the complex C-C bond formation process mediated by living organisms for the selective production of multi-carbon products [1,5–9]. In recent years, the biohybrid systems integrating microorganisms with man-made semiconductors offer new opportunities for the solar-driven CO_2 -to-chemical conversion by taking advantages of both photo- and bio-catalysis [10–13]. To improve the performance of

the artificial photosynthetic system, there is an urgent need for ideal photocatalysts with suitable band gap for visible light absorption, sufficient reductive potential of the conduction band electrons for bio-catalysis, and high biocompatibility for bacterial growth.

Over the past few years, the CdS with a band gap of ca. 2.4 eV is one of the most prominent photocatalysts in the development of biohybrid systems because of its high visible light harvesting capacity, good charge carrier mobility, and suitable band edge potentials [14–17]. However, the chemical-producing rates of the biohybrid systems based on pristine CdS are still unsatisfactory owing to the rapid recombination of photogenerated electron-hole pairs and high energy barrier at surface sites [18,19]. In addition, the release of Cd^{2+} caused by intrinsic photocorrosion could interfere with the biocatalytic process by replacing the metal core of functional enzymes, and even lead to toxic effects on living cells, thereby affecting the sustainability of CO_2 conversion by the biohybrid systems [20]. Therefore, it is desired to overcome the inherent limitations of pristine CdS through regulating its optical property to

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improve the photosynthetic activity and stability of biohybrid systems.

Currently, some strategies, including heterojunction constructing, heteroatom doping, and defect engineering, have been investigated for successfully tuning the features and activities of transition metal sulfide photocatalysts [21–23]. Thereinto, constructing heterojunctions at the nanoscale through the introduction of heteroatoms has been proved as an effective route to optimize electron transfer pathway and promote separation of photogenerated electron-hole pairs [21,24,25]. However, it remains a great challenge to precisely tailor the heterojunctions in composite photocatalysts to obtain the band structure of semiconductors that meet the needs of photosynthetic application [26]. Noteworthily, the twin-induced homojunctions in solid solutions has recently emerged as a type of structure that enables efficient separation of the photogenerated electron-hole pairs [27]. Specifically, as planar defects formed within monocrystalline semiconductor, twin boundaries occur periodically with a constant spacing and long-range order, resulting in the generation of myriad homojunctions in a specific dimension [28–30]. In particular, the electrical resistivity of crystals with high proportion of homojunctions is approximately one order of magnitude lower than that of crystals with routine grain boundaries, thus promoting the transfer of photogenerated carriers within a single crystalline photocatalyst [31]. Moreover, due to its self-building electrostatic field, the enrichment of photogenerated holes could be alleviated [28], thus enabling effective avoidance of metal leaching caused by photocorrosion [32]. More importantly, the twin engineering does not require doping or combination of additional elements, which allows us to tune the band structure of semiconductors in a highly precise manner for specific applications. Therefore, twin engineering is expected to improve the photocatalytic activity and stability of metal sulfide, providing ideal photocatalysts for development of the artificial photosynthetic system. Nevertheless, constructing homojunctions with near periodic and dense distribution by adjusting the bridging mode of crystal phase in metal sulfide for boosting photosynthesis of biohybrid systems has rarely been reported until now.

Considering that CdZnS is one of the most typical semiconductor substrates for twin formation [27,33], the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ s with controllable optical and photoelectric properties were synthesized and applied, for the first time, to the construction of biohybrid systems in this study. Specifically, the unique twin-induced homojunctions with a long-range order were constructed in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanoparticles (NPs) by a hydrothermal method. The synthesized $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ NPs were used as photosensitizers to integrate *Sporomusa ovata* (*S. ovata*), a model acetogenic bacterium [34–36], into a biohybrid system ($\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{S. ovata}$) for light-driven CO_2 conversion. The photosynthetic performance of the as-prepared $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{S. ovata}$ system was systematically evaluated. As expected, it exhibited a superior photosynthetic acetate production activity and stability. The electron generation and transfer in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{S. ovata}$ system were discussed according to various characterizations and density functional theory (DFT) calculations. Moreover, the transcriptome profiles of *S. ovata* in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{S. ovata}$ system in response to light exposure were analyzed to elucidate the underlying molecular mechanism of photosynthesis. This study provided new insights into the design of high-performance artificial photosynthesis platforms for the reduction of CO_2 into chemicals.

2. Materials and methods

2.1. Synthesis of the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$

The twinning $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ s ($x = 0.2, 0.4, 0.6$, and 0.8) were synthesized via a simple hydrothermal method. At room temperature, (n) mmol of $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ ($n = 2, 4, 6$, and 8) and (10-n) mmol of $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 70 mL of deionized water under constant magnetic stirring. Then, 30 mL of fresh Na_2S solution (10 mmol) was slowly added using a micro-injection pump in 30 min for the deposition

of the metal ions. After stirring for 2 h, the obtained yellowish precursor solution was transferred into a 200 mL of Teflon-lined autoclave and maintained at 180°C for 12 h. The precipitates harvested by centrifugation at 8000 rpm for 5 min were washed several times with deionized water and ethanol, and dried at 60°C for 10 h. The final obtained samples were named as $\text{Cd}_x\text{Zn}_{1-x}\text{S}$. Bulk phases of CdS and ZnS were synthesized using the same procedures using $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, respectively, with $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in a molar ratio of Cd/Zn: S = 1: 1.

2.2. Construction of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{S. ovata}$ biohybrid

S. ovata DSM 2662 was purchased from Mingzhou Biotechnology Co., Ltd (Ningbo, China). All culture and sampling manipulations were performed in an anaerobic glovebox with a mixed gas atmosphere of N_2/CO_2 (1.5 atm, 80:20, v/v). *S. ovata* was grown in a sterilized medium (Table S1) that was modified based on ATCC Culture Medium 1425. When the growth stage of *S. ovata* reached the logarithmic phase ($\text{OD}_{545} = 0.25$), $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ was added into the medium to the final concentration of 0.5 mM. After 8 h of cultivation at a magnetic stirring speed of 150 rpm, the medium was sequentially centrifuged at the speed of 8000 rpm for 5 min. The harvested $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{S. ovata}$ biohybrids were thoroughly washed with sterile water three times for further use. The CdS/*S. ovata* and ZnS/*S. ovata* biohybrids were prepared by the same method as controls.

2.3. Photosynthesis reaction

Each biohybrid resuspended with 50 mL of sterilized photosynthetic medium (Table S2) was added into a 125 mL of serum bottle. Cysteine (0.25 wt%) was selected as a sacrificial agent to quench the hole pair. Each bottle was magnetically stirred (120 rpm) at 30°C and irradiated by an in-house fabricated circular LED array composed of violet LEDs ($450 \pm 5\text{ nm}$) for blue light measurements at a light intensity of 20 W m^{-2} .

2.4. Measurement of the photosynthetic products

The photosynthetic products were analyzed by proton nuclear magnetic resonance (^1H NMR, 500 M Avance III spectrometer, Bruker, Germany) spectroscopy with sodium 3-(trimethylsilyl)-2,2',3,3'-tetra-deuteriopropionate (TMSP-d4) as the internal standard. The ^{13}C -isotope labeling experiment was conducted in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{S. ovata}$ system with $\text{NaH}^{13}\text{CO}_3$ as sole carbon source.

The quantum efficiency was determined by the ratio of the effective electrons used for acetate production to the measured photon flux. The reduction of two CO_2 molecules to one acetate molecule requires 8 electrons, giving the following quantum efficiency (QE) equation:

$$\text{QE}(\%) = \frac{8 \times C_a \times V \times N_A}{\Phi_{\text{ph}} \times t \times A} \times 100\%$$

Where,

C_a = total acetate concentration (mol).

V = total suspension volume.

Φ_{ph} ($\text{cm}^{-2}\text{s}^{-1}$) = photo flux.

A (cm^2) = area of illumination.

t (s) = reaction time (t).

N_A = Avogadro's Number (6.022×10^{23}).

2.5. Characterization

Detailed information was provided in the [Supporting Information](#).

2.6. Transcriptomic analysis

Triplicate *S. ovata* cells were harvested from the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system (marked as the Light) and heterotrophic cultures with addition of betaine (marked as the Control), respectively. The RNA preparation, library construction, and sequencing on a BGISEQ-500 platform were performed at the BGI Genomics Institute. The transcriptomic data were analyzed according to the previous reports [37].

3. Results and discussion

3.1. Characterization of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system

The construction and performance of $\text{Cd}_x\text{Zn}_{1-x}\text{S}/S. ovata$ system for photosynthesis were briefly described in Fig. 1a. Firstly, the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ semiconductors were synthesized by the hydrothermal reaction of corresponding metal ions. The actual molar ratios of Cd and Zn elements in the samples were detected by inductively coupled plasma mass

spectrometry (ICP-MS), which were close to the additive proportion (Table S3). The crystal structures of all prepared samples were analyzed by X-ray diffraction (XRD). As shown in Fig. 1b, the bulk phase of ZnS was identified as the typical cubic (PDF#77-2100), while the bulk phase of CdS was identified as a mixture of the cubic and hexagonal (PDF#89-0440 and PDF#01-0780) [33,38]. It is worth noting that the XRD features of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ gradually and consistently shifted from those of ZnS to CdS as the Cd content increased, demonstrating the successful formation of solid solutions in $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ (Fig. S1). The characteristics of multiphase in $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ suggested the possible formation of wurtzite-sphalerite phase-junctions [33]. Furthermore, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were recorded to characterize the morphology and microstructure of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$. SEM image of the optimized $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ (demonstrated in the following part) revealed the uniform morphology of NPs (Fig. 1c). Moreover, the corresponding energy dispersive X-ray spectrometry (EDS) elemental mappings identified the homogeneous distributions of Cd, Zn, and S (Fig. 1c). Low magnification TEM image

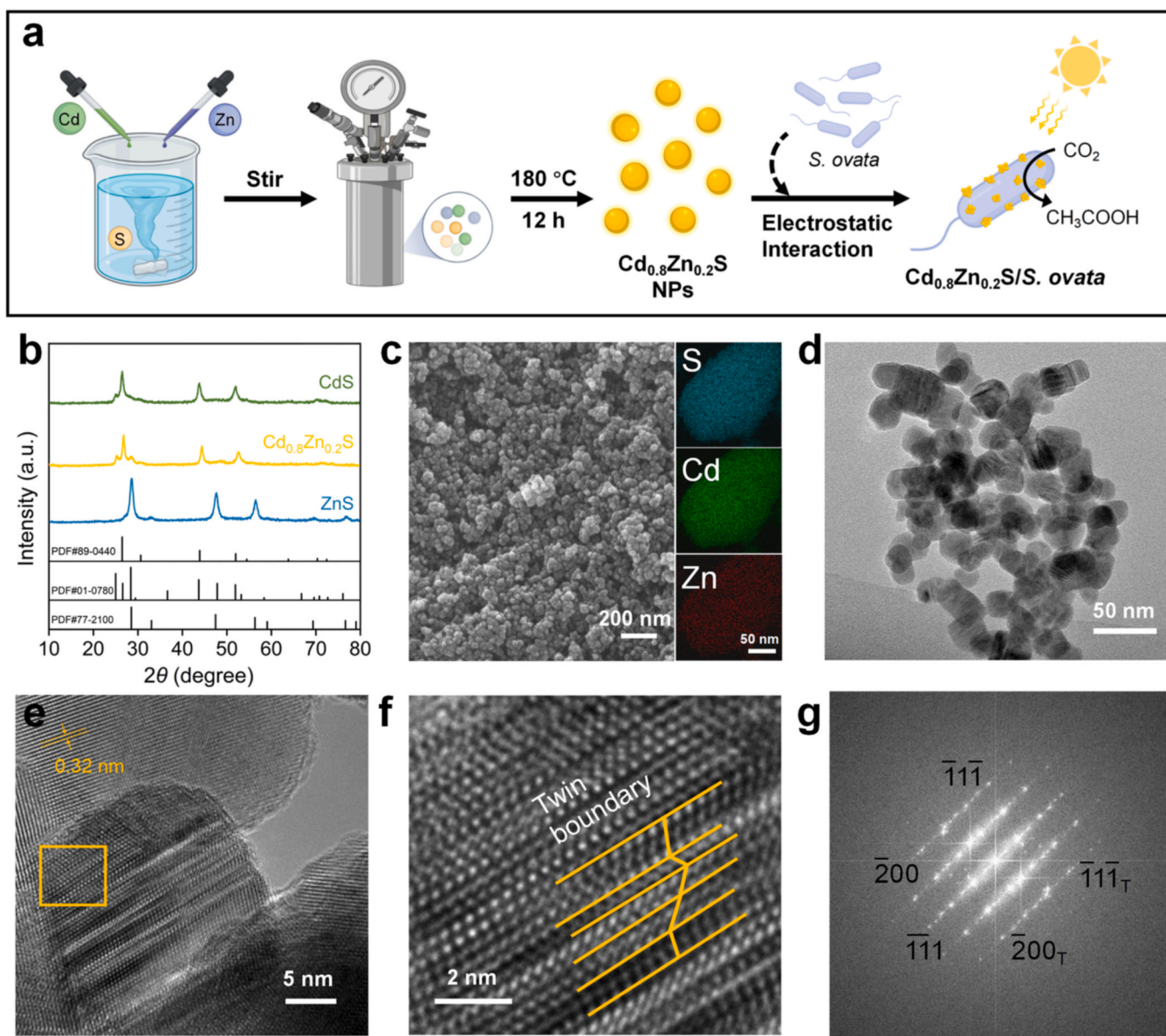


Fig. 1. (a) Schematic illustration for the construction of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system. (b) XRD patterns of the CdS, ZnS, and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$. (c) SEM image and the corresponding EDS element (S, Cd, and Zn) mappings of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$. (d) TEM image of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$. (e) HRTEM image of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$. (f) HRTEM image of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ showing twin boundary. (g) The SAED pattern of twin boundary in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$.

(Fig. 1d) showed consecutively distributed $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ NPs with well-proportioned particle size (20–30 nm). High resolution TEM (HRTEM) image showed the lattice spacing of 0.32 nm, which corresponds to (111) plane of zinc-blende lattice (Fig. 1e) [39]. The abundant existence of zigzag structures and parallel dislocations composed of coherent twin boundaries indicated the twin crystal structures (Fig. 1f). The formation of the nanoscale twin crystal structure was also supported by the unique diffraction features from the selected area electron diffraction (SAED) pattern (Fig. 1g), wherein ordered spots appearing at the sites one-third from the normal spots were attributed to the deviated atoms after twinning from the original sites [26,40]. These results substantially confirmed the formation of solid solutions and excluded the possibility of phase segregation between CdS and ZnS in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ NPs.

X-ray photoelectron spectroscopy (XPS) high-resolution spectra of Cd 3d, Zn 2p, and S 2p were analyzed to reveal the chemical environment of the elements (Fig. S2). With the increase of Cd/Zn ratio, the binding energy of Cd 3d and S 2p gradually shifted towards that of pure CdS, which suggested the formation of Cd–S bonds in the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ NPs. Meanwhile, Zn 2p peaks also negatively shifted, indicating that valence electrons were drawn by the CdS component. This probably favored the photocatalytic performance of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ in the range of visible light [22,41]. The optical absorption properties of the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ were investigated by UV–vis diffuse reflection spectroscopy (UV–Vis DRS). The ZnS showed a narrow UV absorption range, while CdS displayed a broad visible light absorption range from ca. 400–600 nm (Fig. S3). In $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ s, the presence of Cd led to the red shifts of the absorption edges from ca. 500–600 nm, suggesting that these solid solutions were endowed with characteristics of response to

the visible light. The measured direct band gaps of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ s were in a range from 2.33 to 2.49 eV (Fig. S4 and Table S4), which were between that of pure CdS (2.12 eV) and ZnS (3.39 eV). It demonstrated that the light absorption capacities of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ were readily controlled by adjusting the Cd/Zn molar ratios.

For a semiconductor photocatalyst used in the artificial photosynthesis systems, it is critical to increase the generation rate of electron-hole pairs and the half-life of the generated electrons. Photoelectrochemical tests demonstrated that the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ possessed the highest electron-hole pair yield compared with other $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ s (Fig. S5a), accordingly, the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ showed the best photocatalytic acetate production in the biohybrid system (Fig. S5b). Based on this, the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ photosensitizer was applied to incubate with *S. ovata* for construction of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system (Fig. 1a). The zeta potential of *S. ovata* suspension was positively shifted from -38.17 to -32.67 mV after hybridizing $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ NPs with a positive potential of 25.32 mV, indicating that $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ NPs accumulated on the surface of *S. ovata* through electrostatic interactions. XRD patterns of the developed biohybrids further suggested the successful assembly of different photocatalysts on *S. ovata* without detectable changes in their phase structures (Fig. 2a). SEM, TEM and TEM-EDS elemental mapping images showed that the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ NPs were bound to the cell surface of *S. ovata* in clustered or dispersed form (Fig. 2b–d), while these bacterial cells retained their initial sizes and shapes (Fig. S6), suggesting a good biocompatibility of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ NPs to *S. ovata*. It was further confirmed by the unaffected growth kinetic of *S. ovata* in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system (Fig. S7). The metal leaching results showed that no metal ions were characterized after 24 h of illumination (Table S5). In addition, SEM and XRD results indicated that the

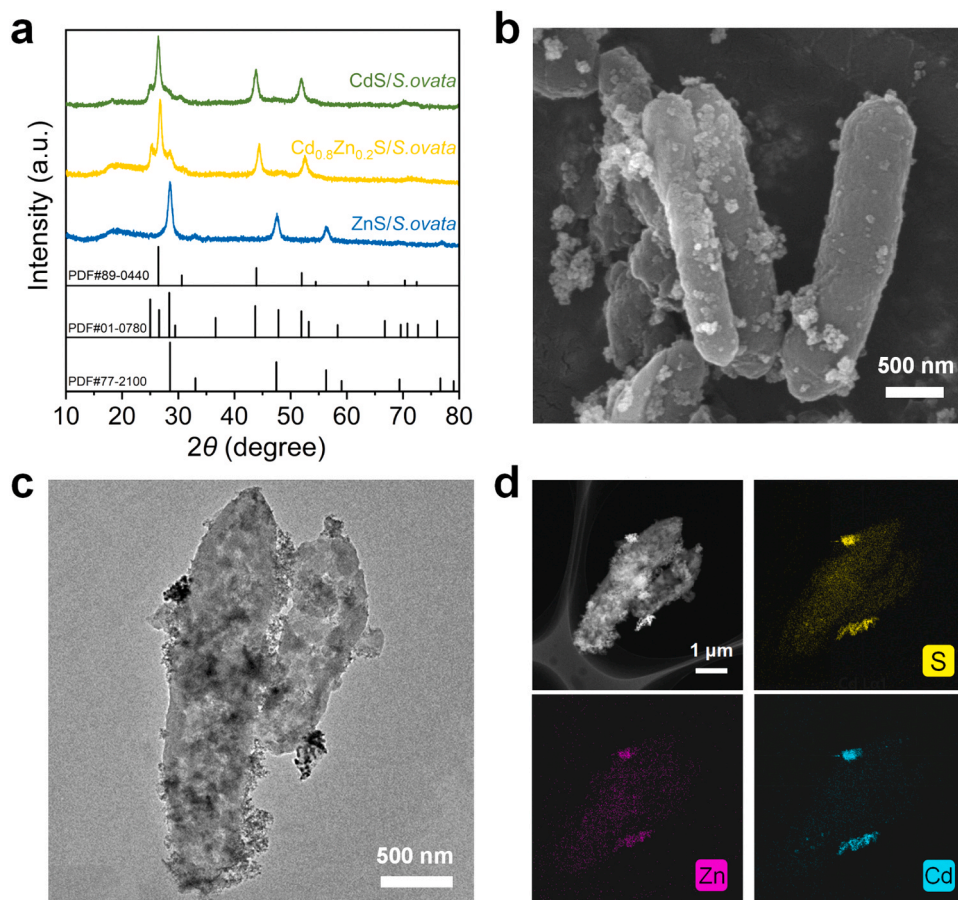


Fig. 2. (a) XRD patterns of the CdS/*S. ovata*, ZnS/*S. ovata*, and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ biohybrids. SEM (b), TEM (c), and TEM-EDS elemental mapping (d) images of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ biohybrids.

$\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ biohybrids still maintained its initial structural characteristics after illumination (Fig. S8 and S9). These demonstrated a great stability of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ in the biohybrid system. Compared to the photocorrosion prevalent in monometallics, bimetallic sulfur-bridge bonds effectively inhibit metal leaching that could lead to reduced biocatalytic activity [20,42]. These evidences suggested the successful construction of a stable photo-responsive $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system, in which *S. ovata* has a potential to realize CO_2 conversion through harvesting photoexcited electrons from the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ NPs under illumination (Fig. 1a).

3.2. Photosynthesis of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system

To investigate photosynthesis of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system, the prepared biohybrids were cultivated under the irradiation of LED light source (450 ± 5 nm) at 35 ± 2 °C. Cell numbers determined by colony-forming unit (CFU) assays suggested that *S. ovata* in the biohybrid systems required light to maintain their viability (Fig. S10). Furthermore, compared to the biohybrid systems, the rapid decline in survival rate of bare *S. ovata* under light-exposure condition indicated the photoprotective effect of photosensitizers on bacteria [10,37]. As expected, only the biohybrid systems composed of living bacterial cells and photosensitizers (CdS, ZnS or $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$) could produce acetate in the presence of CO_2 under illumination (Fig. 3a). The acetate yield in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system (35.20 ± 3.28 mM) was significantly higher than those in the CdS/*S. ovata* (26.20 ± 1.33 mM) and ZnS/*S. ovata* (18.69 ± 3.28 mM) system under the same conditions, probably owing to high generation rate of electron-hole pairs and good affinity of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$. Moreover, the ^1H NMR spectra revealed that only acetate

was produced in the conversion of CO_2 , which was attributed to the highly selective CO_2 fixation pathway employed by *S. ovata* (Fig. S11). Specifically, CO_2 was reduced intracellularly to a common biosynthetic intermediate of acetyl coenzyme A, which was ultimately converted to acetic acid as a metabolic waste product and excreted from the cell [43]. Isotope-labeling experiments further demonstrated that the acetate produced by the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system was derived from CO_2 reduction (Fig. 3b).

The effects of photosensitizer concentration and illumination intensity on the photosynthetic efficiency in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system were investigated. Within a certain range, increasing the photosensitizer concentration could provide more photoelectrons to drive the CO_2 fixation in bacterial cells, however, when the concentration of photosensitizer exceeded the threshold (0.5 mM), the acetate production was inhibited (Fig. 3c). On the other hand, the illumination intensity was also critical for the biohybrid systems to perform photosynthesis. Low power density limited the production rate of photo-generated hole-electron pairs, while excessive illumination intensity might lead to the oxidative photodamage to bacterial cells, thus hindering the photosynthetic reaction and subsequently reducing the acetate yield (Fig. S12). A maximum acetate yield of 43.46 ± 2.57 mM was achieved under the optimal condition ($\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ dosage of 0.5 mM and a light intensity of 70 W m^{-2}). To further evaluate the practicability of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system, it was illuminated at a low light intensity (20 W m^{-2}) with successive light/dark (12/12 h) cycles to simulate natural light irradiation (Fig. 3d). Acetate was continuously produced during the light/dark cycles due to the accumulation of metabolic intermediates [19,44]. The turnaround in the rate of acetate production on the second day was attributed to the adaptation process of

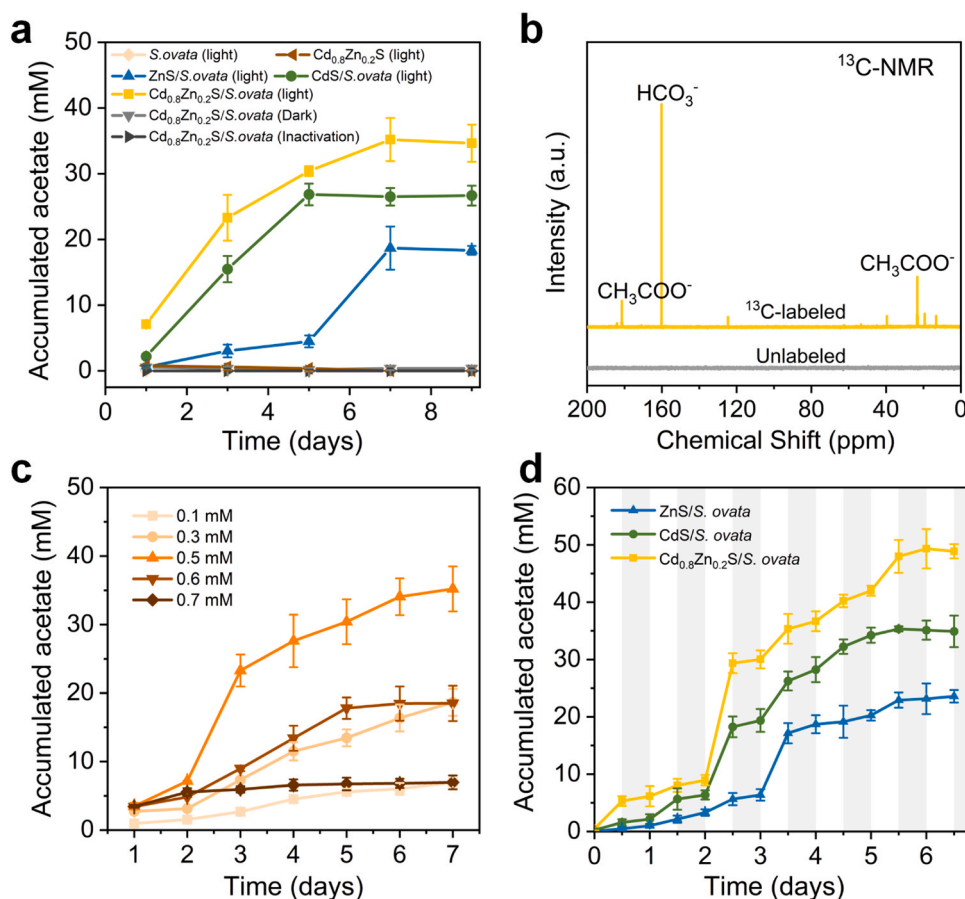


Fig. 3. (a) The yields of acetate in the CdS/*S. ovata*, ZnS/*S. ovata*, $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$, and deletional systems. (b) ^{13}C NMR spectra of the produced acetate with and without $\text{NaH}^{13}\text{CO}_3$ as carbon source. (c) The yields of acetate in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system with different $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ contents. (d) The yields of acetate in the CdS/*S. ovata*, ZnS/*S. ovata*, and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ systems under a continuous light/dark cycle of 12 h.

the bacteria from heterotrophy to photoautotrophy, which was further supported by the corresponding increase in cell viability (Fig. S13). The yield of acetate began to plateau on the sixth day, because of the limited amounts of the sacrificial hole scavenger [19,44]. The maximum yield of acetate reached 49.33 ± 3.54 mM. Notably, the acetate production rate (8.22 ± 0.59 mM d⁻¹) was substantially higher than that of other acetate-producing biohybrid systems (Table S6). In addition, the quantum yield of $16.82 \pm 1.21\%$ was obtained, which exceeded the reported photosynthetic biotic-abiotic hybrid systems (1.6–12.4%) [6,10,44,45]. Multi-cycle experiments showed that the acetate production rate of the Cd_{0.8}Zn_{0.2}S/*S. ovata* system was well maintained over three 6-day cycles (Fig. S14), suggesting its potential for practical applications.

3.3. Twin engineering improved the photoelectron separation and transfer efficiency

To understand the mechanism underlying the excellent performance of the Cd_{0.8}Zn_{0.2}S/*S. ovata* system, the photoelectrochemical property of Cd_{0.8}Zn_{0.2}S, which governs photoelectron separation and transfer, was first evaluated, compared with CdS and ZnS. As shown in Fig. 4a, the Mott-Schottky plots of CdS, ZnS, and Cd_{0.8}Zn_{0.2}S presented positive slopes, proving their n-type semiconductor characteristics [16]. The slope of Cd_{0.8}Zn_{0.2}S was lower than that of CdS and ZnS, indicating an increase in the charge carrier density [16,46]. The high donor density of Cd_{0.8}Zn_{0.2}S demonstrated the dramatically improved charge separation efficiency and electrical conductance because of the twin crystal structure. Moreover, the obviously positive flat-band voltage (E_{fb}) value of the Cd_{0.8}Zn_{0.2}S indicated a less electron-trapping process and higher quantum efficiency compared to the pure CdS and ZnS (Fig. 4a) [47]. To further reveal the photosensitizing behavior of Cd_{0.8}Zn_{0.2}S, photoluminescence (PL) spectroscopy was performed. The pure ZnS exhibited a strong PL emission peak centered at 535 nm due to the charge

recombination induced by surface-defect (Fig. S15) [48]. In comparison, the PL emission spectra of the twinning Cd_{0.8}Zn_{0.2}S and pure CdS gave broad peaks with red shifts, which were originated from the trap-level emissions [21]. In addition, the significant decrease in PL intensity of Cd_{0.8}Zn_{0.2}S indicated that the photo-induced carrier recombination was effectively inhibited [49]. Time-resolved photoluminescence (TR-PL) decay spectra (Fig. 4b) were obtained to evaluate the charge separation efficiency. The average PL lifetime values (τ_{ave}) of Cd_{0.8}Zn_{0.2}S, CdS, and ZnS were calculated to be 71.79, 40.61, and 59.70 ns, respectively (Table S7). The high efficiency of photoelectron separation on the surface of Cd_{0.8}Zn_{0.2}S was beneficial for electron transfer from the light-excited Cd_{0.8}Zn_{0.2}S to the energy harvesting system of *S. ovata*. These results were further corroborated by the chronoamperometric I-T curves with repetitive on/off cycles of irradiation, where the Cd_{0.8}Zn_{0.2}S/*S. ovata* biohybrid showed substantially higher photocurrent intensity than the CdS/*S. ovata* and ZnS/*S. ovata* biohybrids (Fig. 4c). Moreover, the current of CdS/*S. ovata* biohybrid decreased over time likely due to the rapid recombination of electrons and holes in the pure CdS [50]. This was in agreement with the PL results, in which the average PL lifetime of pure CdS was shorter than that of ZnS and Cd_{0.8}Zn_{0.2}S, suggesting a remarkable short-lived charge separation (Table S7). The Nyquist plots were obtained to analyze the charge transfer kinetics. The Cd_{0.8}Zn_{0.2}S/*S. ovata* exhibited a smaller interfacial resistance (R_{ct}) compared to the CdS/*S. ovata* and ZnS/*S. ovata*, confirming a faster interfacial electron transfer in the Cd_{0.8}Zn_{0.2}S/*S. ovata* biohybrid under illumination (Fig. 4d). These results illustrated that the Cd_{0.8}Zn_{0.2}S with twin-induced homojunctions could effectively accelerate the generation and transfer of photoelectrons.

The energy level structure in Cd_{0.8}Zn_{0.2}S was investigated to better understand the behavior of electron transfer in the twinning structure. Based on above analysis, the structural configuration (Fig. 4e) and band position (Fig. 4f) for the twinning Cd_{0.8}Zn_{0.2}S were proposed. In general,

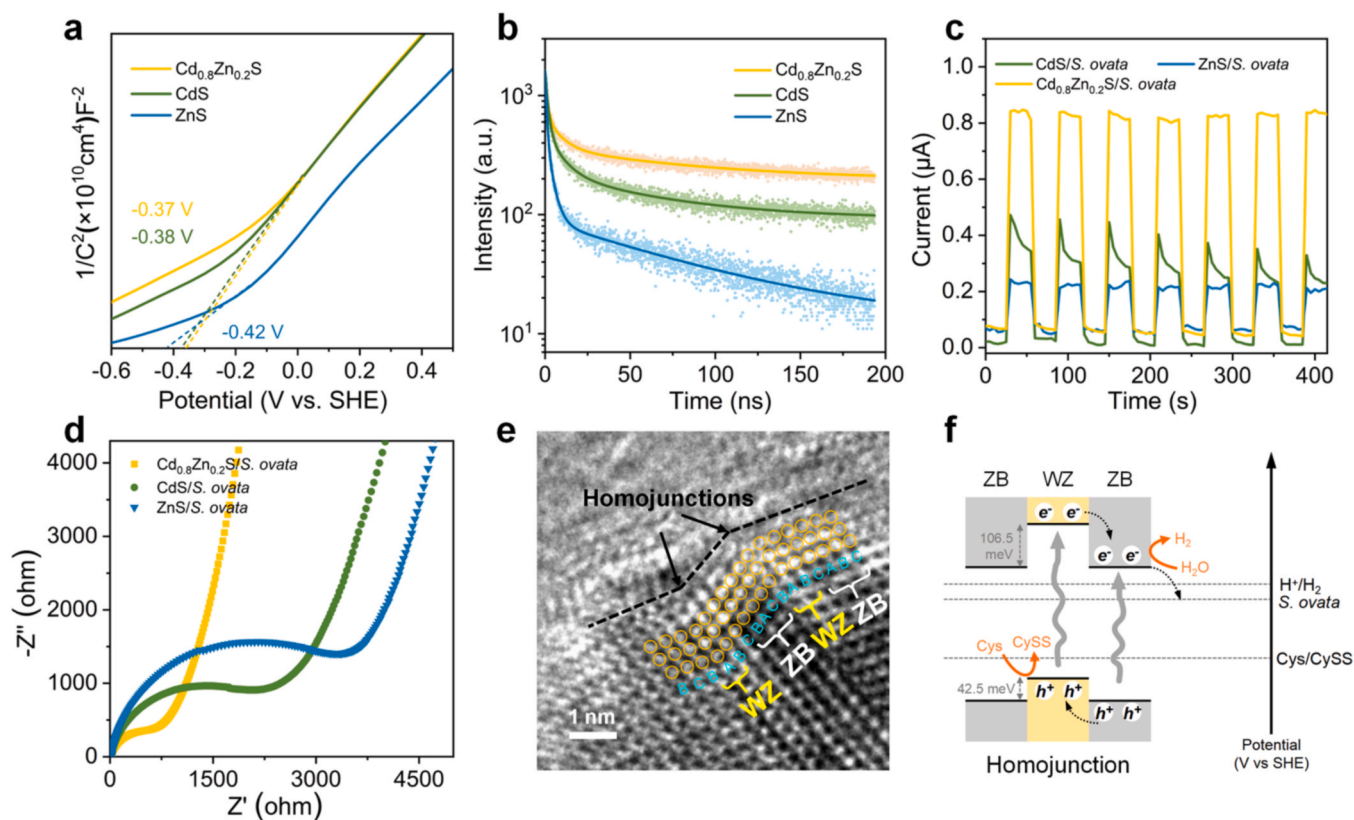


Fig. 4. Mott-Schottky plots (a) and TR-PL decay curves (b) of the CdS, ZnS, and Cd_{0.8}Zn_{0.2}S. (c) I-T curves of the CdS/*S. ovata*, ZnS/*S. ovata*, and Cd_{0.8}Zn_{0.2}S/*S. ovata* biohybrids under a light on/off cycle. (d) Nyquist plots of the CdS/*S. ovata*, ZnS/*S. ovata*, and Cd_{0.8}Zn_{0.2}S/*S. ovata* biohybrids. (e) Atomic scale image of twin-induced homojunctions in the Cd_{0.8}Zn_{0.2}S. (f) Mechanism for photogenerated charge separation in the homojunction of Cd_{0.8}Zn_{0.2}S. Cys, cysteine. Cyss, cystine.

binary compounds with close-packed crystal structures can crystallize into zinc-blende (ZB), wurtzite (WZ), and a mixture of them [27]. When stacking faults are introduced, the otherwise ordered ZB and WZ structures may be disrupted [26]. As shown in Fig. 4e, the misplacement of ZB layer in the (111) direction formed a twin plane with mirror-symmetric structures, in which the misaligned lattice sequences (e.g., BAB arrays) could be considered as a WZ structure [51,52]. As a result, the appearance of these twin planes in nanocrystals broke the continuous ZB lattice constitution and created numerous WZ segments [26]. Specifically, periodic light/dark contrast resulted from alternating twins along the (111) crystalline direction of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ NPs could be clearly observed (Fig. 4e). Furthermore, the average band gap of the twinning $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ nanocrystals was determined to be 2.62 eV. The conduction band (CB) and valence band (VB) positions were calculated to be -0.579 and 1.751 eV (Fig. 4f), which could effectively drive photocatalytic hydrogen evolution (-0.41 V vs. SHE) [53] and cysteine oxidation (1.04 V vs. SHE) [54], respectively. More importantly, the WZ $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ was demonstrated to occupy higher CB and VB positions than its ZB counterpart [26,55]. Therefore, a large amount of homo-junctions consisting of two phases (ZB and WZ) in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$

offered gradient built-in electric fields, resulting in highly efficient separation and migration of photogenerated electron-hole pairs (Fig. 4f).

To further elucidate the role of active sites in electron transfer at the biotic-abiotic interface, density functional theory (DFT) calculation was conducted. The DFT calculations of the energy band structure (Fig. 5a-c) and density of states (Fig. 5d-f) revealed the typical semiconductor features of CdS, ZnS, and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$. The $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ possessed a significantly higher charge density than CdS and ZnS at the Fermi energy level, which contribute to an excellent conductivity. The differential charge density distribution in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ were showed in Fig. 5g, where the yellow and light blue parts represented charge accumulation and depletion, respectively. Apparently, the electrons in the region of S atoms were accumulated by the electron loss and transfer of on the Cd and Zn atoms, whereas there was no diffusion of electrons around the S atoms, forming a stable charge transfer process. In addition, the Gibbs free energy of H atom adsorption by CdS, ZnS, and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ was calculated (Fig. 5h). The ΔG_{H^*} value (0.22 eV) was significantly lower after the formation of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ solid solution (Fig. 5i), which was favorable for photocatalytic hydrogen production [49]. The ΔG_{H^*} values

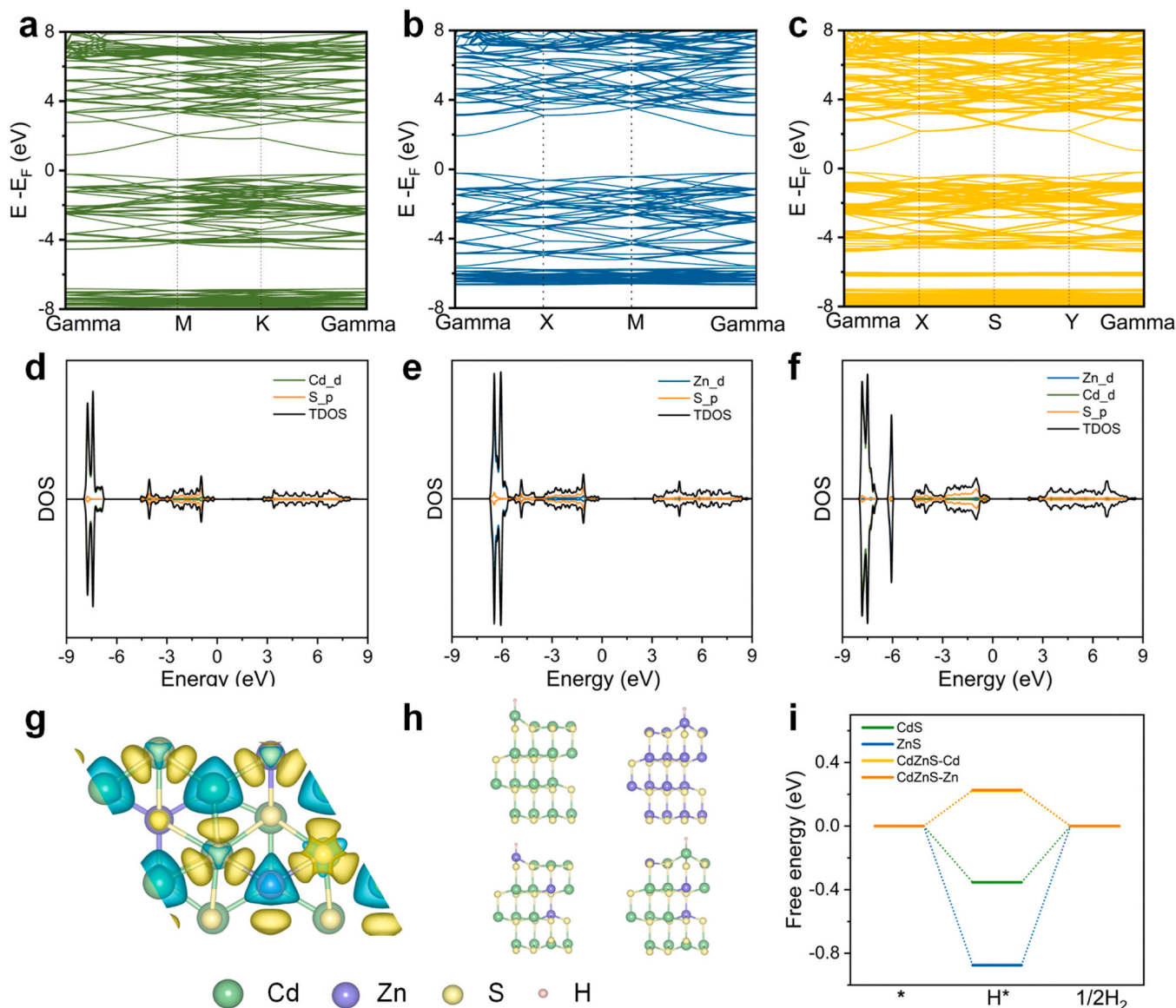


Fig. 5. Energy band structure (a-c) and density of states (DOS) (d-f) of the CdS, ZnS, and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$. Charge density difference (g) and schematic structure model (h) of H adsorption by the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$. (i) Free energy diagrams of reaction of CdS, ZnS, and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$.

at active sites of CdS and ZnS were -0.36 and -0.87 eV, respectively, suggesting too strong adsorption of H atom on the surface that hindered hydrogen diffusion [56]. DFT results suggested that an optimal surface could be formed by the replacement of Cd sites with Zn atoms, while a lower or higher Zn concentration would lead to an insufficient number of active sites or even formation of inactive sites. With the formation of H atoms from water or protons via photoexcited electrons, the ideal adsorption and desorption environment of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ favored the hydrogen escape from the active sites to *S. ovata*. This could be a potentially important factor resulting in the improved acetate production in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system, as discussed in the following section.

3.4. Mechanism underlying photosynthetic acetate production in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system

To gain insight into the molecular mechanism underlying photocatalytic CO_2 conversion, triplicate *S. ovata* cultures under photoautotrophic ($\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{light}/\text{CO}_2$) and heterotrophic (betaine/ CO_2) conditions were collected for transcriptome analysis. The score plots of principal component analysis (PCA) showed that transcriptome from $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ -fed and betaine-fed *S. ovata* were clustered into discriminative groups with 95% confidence (Fig. 6a). This result suggested that the photoexcited $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ significantly affected the physiological state of *S. ovata* in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system. The differentially expressed genes (fold change (FC) > 1.5 and p value < 0.05), including 1098 of the up-regulated and 1051 of the down-regulated, were identified in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ -fed group compared to the heterotrophic group (Fig. 6b and Supplementary Data S1). The Kyoto Encyclopedia of Genes and Genomes database was used for the analysis of biological pathways. The results showed that the expression of most genes associated with electron transfer, energy conversion, and CO_2 fixation was significantly up-regulated in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system, which was considered to be responsible for the photosynthesis.

In addition to the fast kinetics observed on the semiconductor

photocatalyst, the key to the operation of the biohybrid system is the interaction of the microbial catalyst with these external donors, which allows for synergistic electron harvest and carbon metabolism [6,57]. The membrane-associated proteins play important roles in direct electron transfer [43]. The up-regulated genes encoding membrane-bound flavoproteins (Fp), cytochromes, and ferredoxin (Fd) revealed that the electrons from photoexcited $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ could be transferred through these proteins into *S. ovata* for subsequent conversion of CO_2 (Fig. 6c and Table S8) [58]. It was further confirmed by the results of membrane protein assay, which showed that the normalized concentrations of membrane-bound proteins in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system significantly increased after illumination (Fig. S16). Specifically, Fp is considered to be the key membrane-integrated electron carrier and plays a major role in the electron transfer [4,58]. Cyclic voltammetry (CV) curve of *S. ovata* showed a dominant redox center with a mid-potential of -0.48 V (vs. SHE), which could be assigned to Fp distributed on the cell membrane (Fig. 7a) [4,59]. Compared with pure *S. ovata*, a higher peak current of the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ under illumination indicated that the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ improved the electron transfer in the biohybrid system. The introduction of biocompatible $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ did not significantly alter the electron transfer pathway of *S. ovata*, but promoted the formation of membrane-bound redox active mediators. Furthermore, the reduction potentials of the photoexcited $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ were higher than that of the redox active mediators, ensuring that *S. ovata* could efficiently harvest photoelectrons through membrane proteins. Given Fp had a more negative redox potential than $\text{NAD(P)}^+/\text{NAD(P)H}$ couple (-0.32 V) [58], the electrons obtained by *S. ovata* could be utilized to produce the universal electron donors (NADH and NAD(P)H) for intracellular CO_2 conversion.

Moreover, the genes of membrane-bound [Ni-Fe] hydrogenases and soluble [Fe-Fe] hydrogenase complex (HydABC) for hydrogen production/utilization were significantly up-regulated (Fig. 6c and Table S9) [60]. It indicated that hydrogen might act as an electron donor for cell metabolism [43,61]. The yield of photocatalytic H_2 by $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ after 24 h of illumination was investigated to reach 7.13 ± 0.65 mmol $\text{g}_{\text{cat}}^{-1}$.

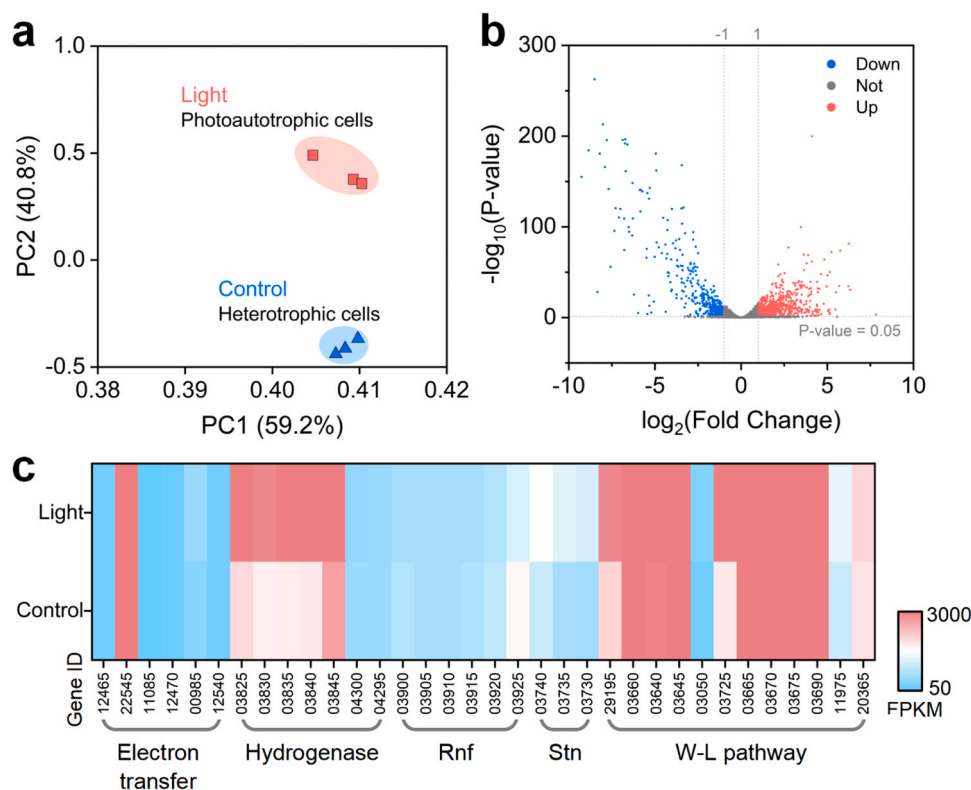


Fig. 6. PCA (a) and volcano plot (b) of the transcriptomic data. (c) Heatmaps of differentially expressed genes.

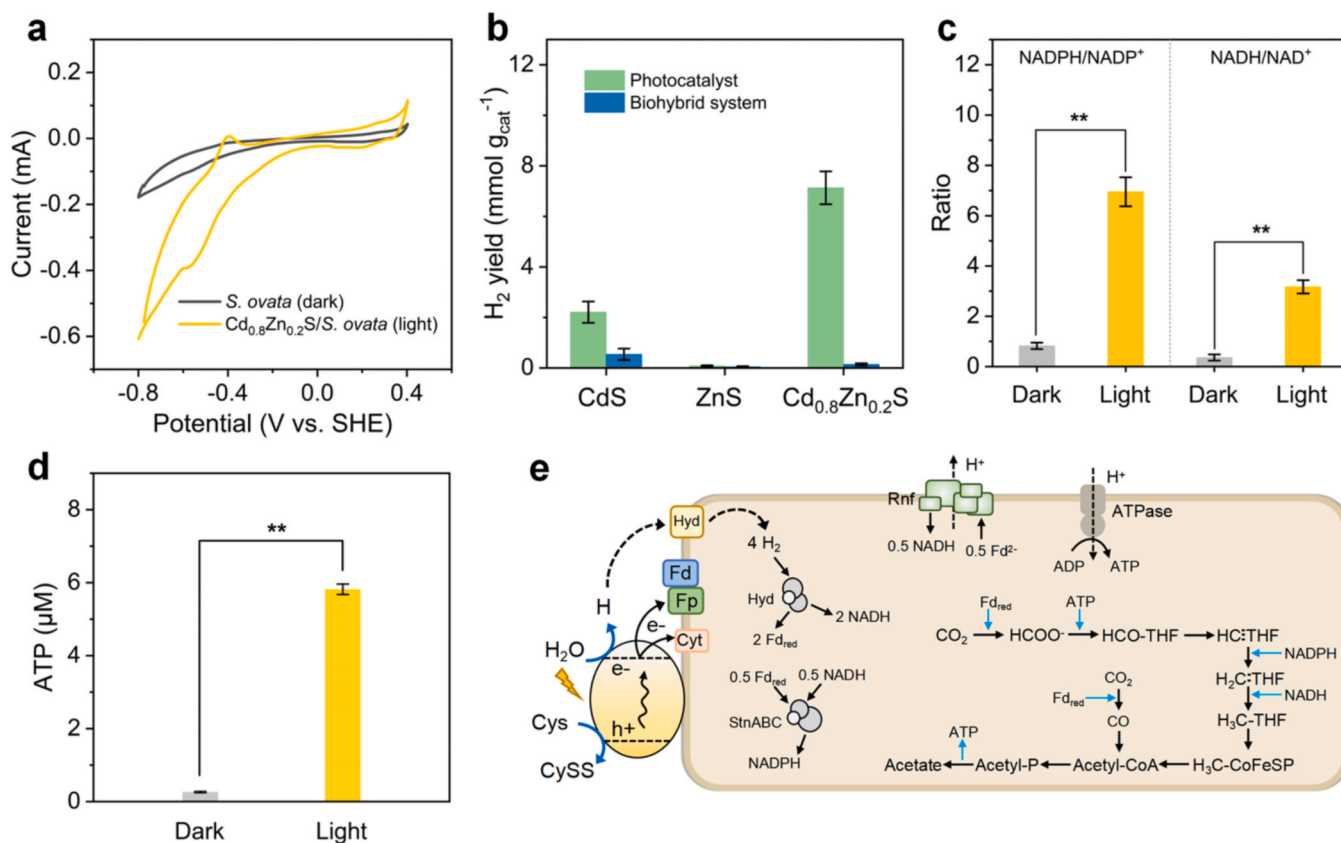


Fig. 7. (a) CVs of the *S. ovata* and Cd_{0.8}Zn_{0.2}S/*S. ovata* biohybrids in 10 mM of phosphate buffered saline solution (pH 7). (b) The initial hydrogen generation rate over CdS, ZnS, and Cd_{0.8}Zn_{0.2}S by 4 h test. NAD(P)H/NAD(P)⁺ ratio (c) and ATP concentrations (d) in the Cd_{0.8}Zn_{0.2}S/*S. ovata* system under different conditions. (e) Proposed mechanism of photosynthesis in the Cd_{0.8}Zn_{0.2}S/*S. ovata* system. Cys: cysteine. Cyss:cystine.

which was 3.2- and 83.8-fold higher than that of CdS and ZnS, respectively (Fig. 7b), suggesting the synergistic cooperation of Cd and Zn sites in Cd_{0.8}Zn_{0.2}S for high production of H₂. In contrast, a negligible H₂ yield was observed in all biohybrid systems under illumination, demonstrating that the produced H₂ could be harvested by *S. ovata* for CO₂ reduction. However, H₂ cannot be completely consumed by *S. ovata* due to its low solubility and high utilized concentration threshold [45, 62]. According to the optimal binding energy of H atom at active sites of Cd_{0.8}Zn_{0.2}S and the tight bonding of Cd_{0.8}Zn_{0.2}S and *S. ovata*, the formed H atoms on the surface of photoexcited Cd_{0.8}Zn_{0.2}S could be effectively transferred from active sites to *S. ovata* for CO₂ reduction, thus avoiding H₂ evolution as a side reaction [45].

The H atoms transferred from active sites of Cd_{0.8}Zn_{0.2}S or possibly a small amount of produced H₂ drove the simultaneous reduction of Fd and NAD⁺ to Fd_{red} and NADH, respectively, through hydrogenases. Subsequently, the overexpressed Nfn-type transhydrogenase (Stn complex) catalyzed the electron bifurcation from Fd_{red} and NADH to NADP⁺ (Fig. 6c and Table S10). In addition, the Fd_{red} could be used by the ferredoxin:NAD⁺ oxidoreductase (Rnf complex) for the reduction of NAD⁺, thereby generating a H⁺-gradient across the membrane for ATP generation (Fig. 6c and Table S10). As expected, the increased NAD(P)H/NAD(P)⁺ ratio and ATP concentration were detected in the Cd_{0.8}Zn_{0.2}S/*S. ovata* system under illumination (Fig. 7c,d). The generated intracellular electron donors and ATP could drive the CO₂ fixation pathway of *S. ovata* for CO₂ reduction. Specifically, all necessary enzymes in the Wood-Ljungdahl (W-L) pathway for CO₂ fixation were significantly up-regulated in the Cd_{0.8}Zn_{0.2}S/*S. ovata* system (Fig. 6c and Table S11), which supported a high yield of acetate through photosynthesis.

The reactive oxygen species (ROS) generated under illumination is an important factor affecting the bacterial viability in the biohybrid

systems [44]. It was found that the genes encoding superoxide dismutase and catalase [63] were up-regulated, which activated a survival response to the ROS stress of *S. ovata* in the Cd_{0.8}Zn_{0.2}S/*S. ovata* system (Table S12). Furthermore, the ROS levels in the cytoplasm of *S. ovata* were tested through a ROS assay kit. The result showed that the ROS concentration in pure *S. ovata* was 2.6 times higher than that in Cd_{0.8}Zn_{0.2}S/*S. ovata* after illumination for 24 h (Fig. S17). This revealed the beneficial effect of Cd_{0.8}Zn_{0.2}S on eliminating ROS, which might be attributed to its multiple energy levels that promoted the neutralization of the active species to stable states [64]. These results confirmed that the cells integrated with Cd_{0.8}Zn_{0.2}S possessed a stronger resistance to oxidative damage compared to pure *S. ovata*, contributing to the long running time of the Cd_{0.8}Zn_{0.2}S/*S. ovata* system.

Conclusively, the pathways for electron and proton transfer toward acetate production in the Cd_{0.8}Zn_{0.2}S/*S. ovata* system were proposed (Fig. 7e). Initially, the Cd_{0.8}Zn_{0.2}S was excited to produce the electron-hole pairs under visible light. Due to the presence of twin-induced homojunctions, the photogenerated electrons and holes could be spatially transferred to the ZB and WZ regions, respectively, thus effectively separating the photogenerated electron-hole pairs. The holes were subsequently quenched through the oxidation of cysteine. The conduction band electrons might be transferred to *S. ovata* via hydrogen- and membrane-bound protein-mediated electron transport pathways, thereby generating excessive intracellular electron donors. In addition, ATP synthesis was driven by the proton motive force generated through the transmembrane Rnf complex. Finally, the resulted high energy reducing equivalents and ATP were passed on to the W-L pathway for efficient synthesis of acetate from CO₂ conversion.

4. Conclusions

In conclusion, twinning $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ solid solutions with dense distribution of homojunctions were synthesized and explored as efficient photosensitizers in the biohybrid system. The designed $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/S. ovata$ system achieved the highest photosynthetic acetate production of $49.33 \pm 3.54 \text{ mM}$ at the production rate of $8.22 \pm 0.59 \text{ mM d}^{-1}$ and the quantum efficiency of $16.82 \pm 1.21\%$. This was attributed to the close interconnection of the zinc-blende and wurtzite phases at the atomic level in the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$, which showed significant advantages in efficient separation of photogenerated electron-hole pairs and prevention of photocorrosion. Furthermore, it was found that indirect and direct electron uptake mediated by hydrogen and membrane-bound proteins (such as cytochromes, ferredoxin, and flavoproteins), respectively, contributed to photoelectron transfer from $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ to *S. ovata* for CO_2 conversion. This work paves a convenient route to design efficient photocatalyst with twin-induced homojunctions for construction of biohybrid systems, and provides insight into the complex interactions between semiconductors and microorganisms.

CRediT authorship contribution statement

Kejing Zhang: Investigation, Data curation, Writing – original draft. **Ruijie Li:** Formal analysis, Investigation, Data curation, Software. **Jianxin Chen:** Investigation, Data curation, Writing – review & editing. **Liyuan Chai:** Supervision, Funding acquisition. **Zhang Lin:** Validation, Writing – review & editing. **Long Zou:** Investigation, Data curation, Writing – review & editing. **Yan Shi:** Conceptualization, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123375](https://doi.org/10.1016/j.apcatb.2023.123375).

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